

N 66-13499	
(ACCESSION NUMBER)	(THRU)
11	1
(PAGES)	(CODE)
TMX 57034	06
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

POLY(IMIDAZOPYRROLONES): A NEW CLASS OF  
RADIATION RESISTANT POLYMERS

By Vernon L. Bell and George F. Pezdirtz

National Aeronautics and Space Administration  
Langley Research Center  
Langley Station, Hampton, Virginia

Presented at the 150th National Meeting of  
The American Chemical Society

Atlantic City, New Jersey  
September 12-17, 1965

GPO PRICE \$ \_\_\_\_\_

CFSTI PRICE(S) \$ \_\_\_\_\_

Hard copy (HC) 1.00

Microfiche (MF) .50

# POLY(IMIDAZOPYRROLONES): A NEW CLASS OF RADIATION RESISTANT POLYMERS

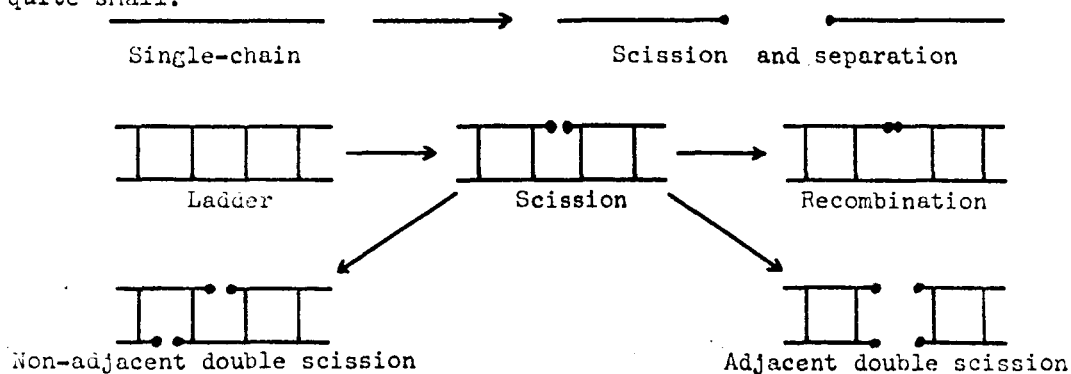
Vernon L. Bell and George F. Pezdirtz

National Aeronautics and Space Administration  
Langley Research Center  
Spacecraft Materials Section  
Langley Station, Hampton, Virginia

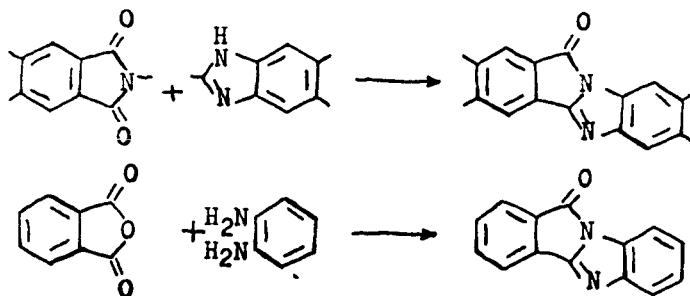
## INTRODUCTION

The development of the polybenzimidazoles<sup>1</sup> and the polyimides<sup>2</sup> represent a major advance in the recent research on high temperature polymers. Numerous other novel polymers<sup>3</sup> have followed which show comparable resistance to heat. One of the primary reasons for the high level of stability of the aromatic-heterocyclic polymers lies in the inherent stability of their fused ring systems; however, potentially weak points in their structures are the single links along the chains. It has been proposed<sup>4</sup> that the preparation of ladder (two-strand) polymers would represent the next plateau in thermally-stable organic polymers. Theoretical studies of the degradation of ladder polymers<sup>5</sup> support this view.

In cases where chain scission is considered to be an equilibrium process, then degradation of single chain polymers will occur with each break in the main chain since the fragmented ends can separate permanently. However, when a break occurs at any point along a ladder polymer, the second strand keeps the entire polymer system intact and the close proximity of the fragmented ends makes recombination probable. Furthermore, the statistical likelihood that a second break will occur adjacent to the first is quite small.



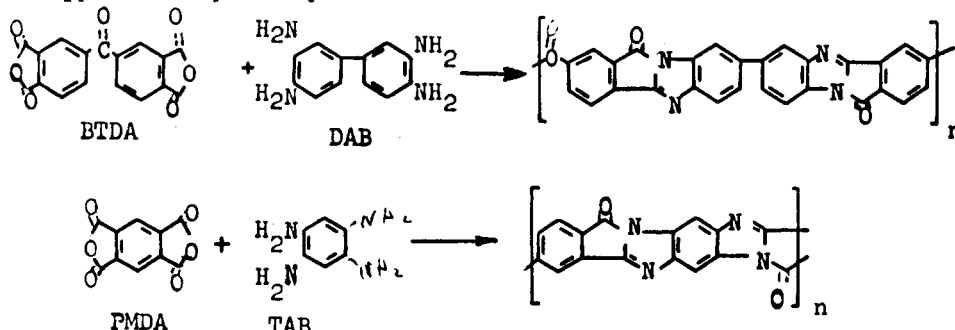
It is apparent that if the single links of the polybenzimidazoles and polyimides are reduced or eliminated by fusing the two structures together, a much greater degree of thermal and radiative stability should result.



## RESULTS AND DISCUSSION

### Synthesis

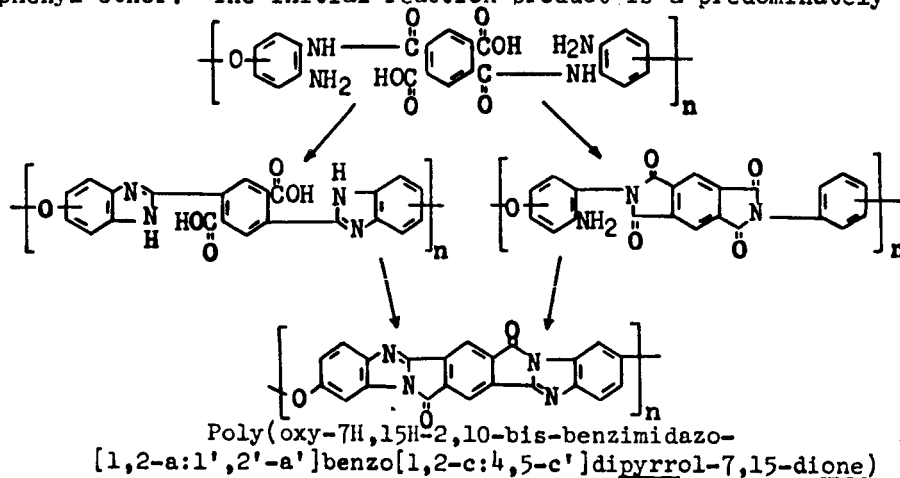
Reactions in classical dye chemistry have resulted in the desired fused ring system, as illustrated by the reaction of phthalic anhydride with o-phenylene diamine.<sup>6</sup> By extending this reaction to dianhydrides and tetraamines with two pairs of ortho-diamines, we have been able to prepare polymers which we have called stepladder (partial ladder) and ladder polyimidazopyrrolones, or "Pyrrones".



An example of a stepladder polyimidazopyrrolone is shown by the reaction of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) with 3,3'-diaminobenzidine (DAB). Since both of these monomers have single junctures in their structures, the resulting polymer structure has only partial ladder character; that is, short ladder segments separated by single bonds. On the other hand, if dianhydrides, such as pyromellitic dianhydride (PMDA) are reacted with tetraamines, such as 1,2,4,5-tetraaminobenzene (TAB), the result is a polymer with a potentially complete ladder structure.

The versatility of this reaction scheme is apparent when one considers the number of copolymers which could result by combining different anhydrides and amines. This allows for variation of the number of the fused rings starting with a minimum of four, and thus makes it possible to control the polymer properties to a certain extent.

The general technique of polymerization involves the carefully controlled reaction of a dianhydride with a tetraamine in highly-polar solvents such as dimethylformamide, dimethylacetamide, and dimethylsulfoxide. The room temperature reaction is extremely rapid and leads to a slight temperature rise, accompanied by an increase in viscosity. Adjustment of the viscosity to the desired level can be accomplished by the addition of small incremental amounts of dianhydride. A proposed mechanism is illustrated below by the reaction of pyromellitic dianhydride with 3,3',4,4'-tetraaminodiphenyl ether. The initial reaction product is a predominately



linear polyamide with unreacted amino and carboxyl groups. This stage is referred to as the A-A-A prepolymer, which exists as a completely soluble dope. When heated, this polymer undergoes two consecutive dehydration-cyclization steps by either or both of two routes, through the polybenzimidazole or polyimide structures, and thence to the final form. Nomenclature derived from Patterson's Ring Index<sup>1</sup> appears to be ample justification for referring to these polymers as "Pyrrones."

Most of the tetraamines can be used as free amines. However, particularly unstable tetraamines, e.g. 1,2,4,5-tetraaminobenzene are more easily handled as the tetrahydrochloride salts. The use of the salt requires an acid acceptor, such as pyridine, to take up hydrochloric acid; otherwise the experimental procedure is the same.

Evidence for the proposed structures of the polymers has been deduced from the infrared spectra of thin films. Figure 1a shows the spectra of a film with a thickness of 0.15 mil which was prepared from pyromellitic dianhydride and tetraaminodiphenyl ether (TADPO), at the A-A-A polymer stage and at the thermally-converted imidazopyrrolone stage. The disappearance of secondary amide bands at 1650, 1540, and 1280  $\text{cm}^{-1}$  is apparent as well as those of carboxyl bands at 1720, 1605, and 1225  $\text{cm}^{-1}$ . The development of imide bands at 1765 and 720  $\text{cm}^{-1}$  along with the appearance of an imidazole band at 1620  $\text{cm}^{-1}$  further support the proposed structure.

Figure 1b shows the similar evidence for the existence of the all-ladder structure of the PMDA-tetraaminobenzene polymer.

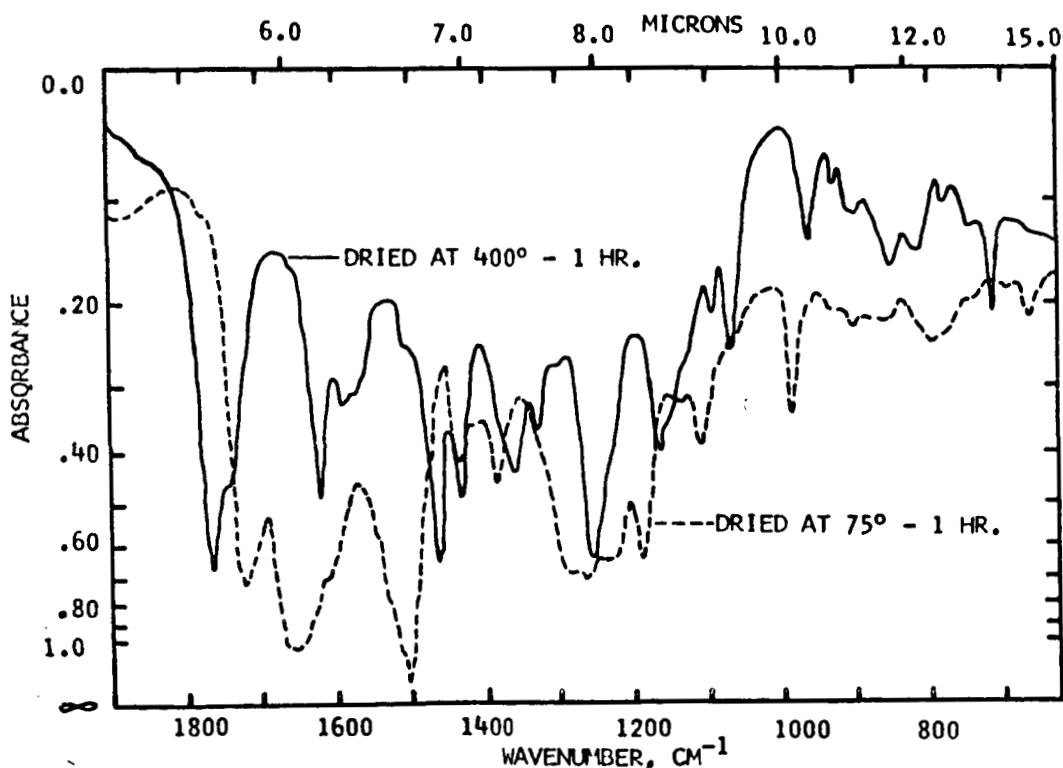


FIGURE 1A. - INFRARED SPECTRA OF PMDA-TADPO POLYMER FILMS, 0.15 MIL THICK

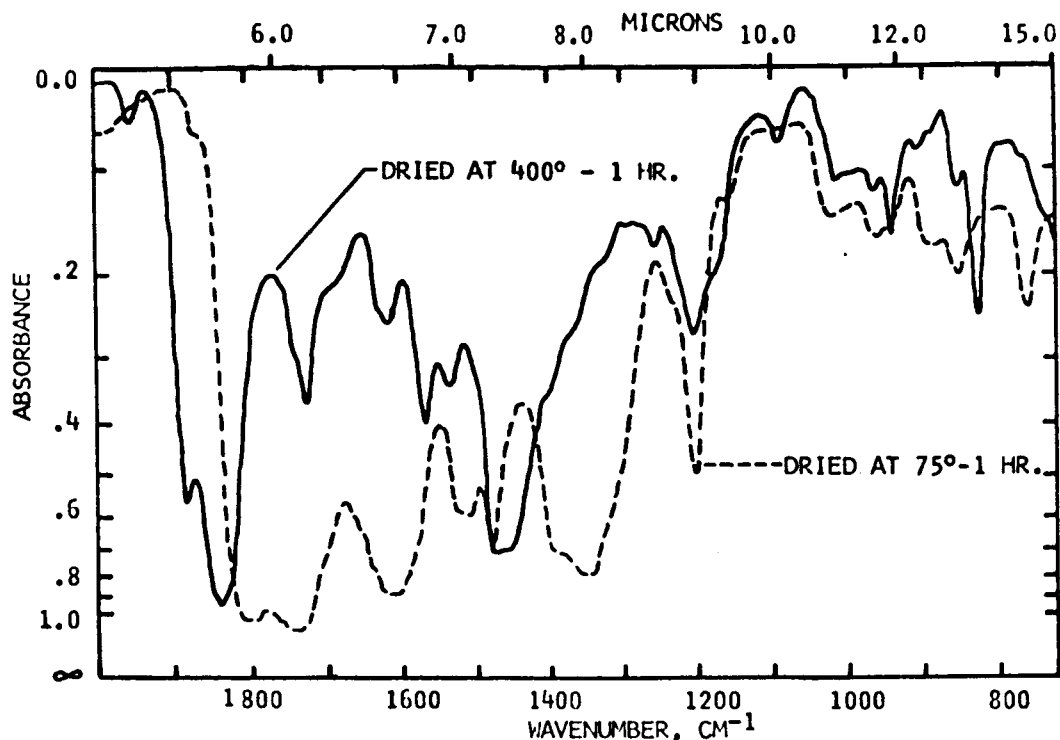


FIGURE 1B. - INFRARED SPECTRA OF PMDA-TAB POLYMER FILMS, 0.15 MIL THICK

Figure 2 shows the loss of amino ( $3355$  and  $3450\text{ cm}^{-1}$ ) and amide ( $3230\text{ cm}^{-1}$ ) nitrogen-hydrogen stretching bands, together with the disappearance of carboxyl oxygen-hydrogen absorption ( $2800\text{ cm}^{-1}$ ) for the pyromellitic dianhydride-tetraaminodiphenyl ether polymer.

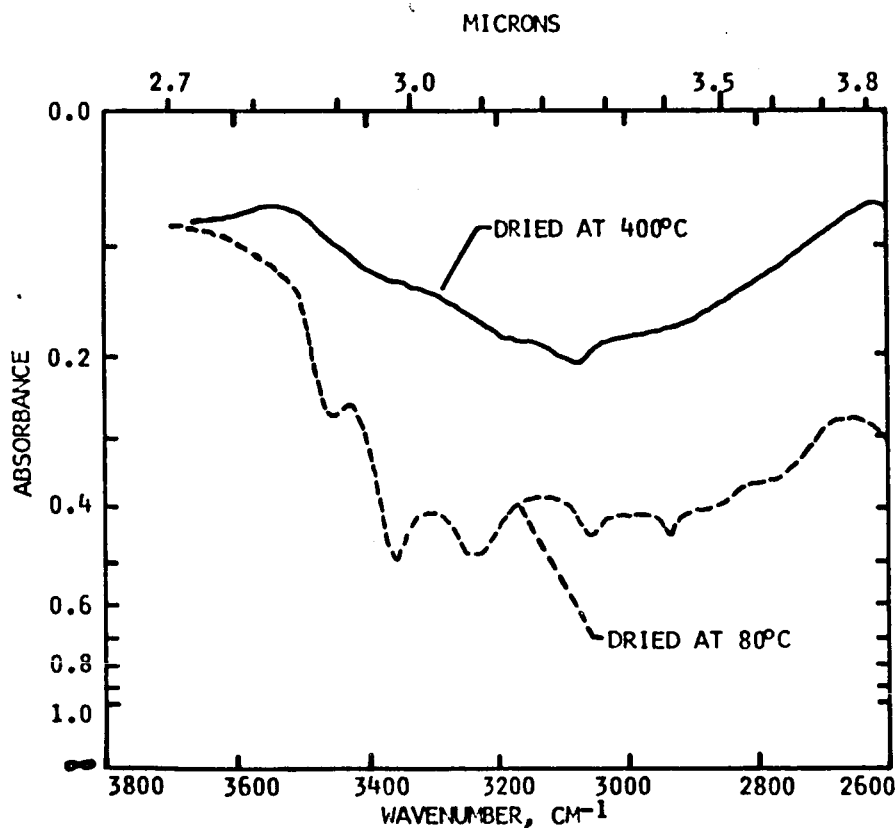


FIGURE 2. - INFRARED SPECTRA OF PMDA-TADPO POLYMER FILMS, 0.15 MIL THICK

## PROPERTIES

Some of the properties of the polyimidazopyrrolones have been listed in Table I. While the final polymer is insoluble and infusible, the excellent solubility of the prepolymer makes it possible to use classical solution techniques for characterization. The solution viscosities of 0.5-1.5 and number average molecular weights of 7,000-20,000 are typical of condensation polymers.

Table I

### Representative Properties of Poly(Imidazopyrrolones)

<u>Solution Properties</u>	<u>A-A-A Stage</u>	<u>Pyrrone Stage</u>
Intrinsic Viscosity (25°, DMF)	0.5-1.5 dl/g.	Insoluble
M <sub>n</sub> (Osmotic Pressure)	7,000-20,000	"
Solvents	DMF, DMAC, NMP, DMSO, etc.	"
<u>Film Properties</u>		
Tensile Strength	10-15 Kpsi	15-22 Kpsi
Elongation	25-35%	3-7%
Young's Modulus	200-400 Kpsi	600-1,000 Kpsi
Specific Resistivity (25°C)	6 x 10 <sup>9</sup> ohm-cm	3-5 x 10 <sup>12</sup> ohm-cm
Field Strength	2 x 10 <sup>5</sup> v/cm	6 x 10 <sup>5</sup> v/cm

The tractability of the A-A-A polymer affords a way to process the polyimidazopyrrolones as thin films, coatings and resins for composite structures. Films have been obtained by casting the A-A-A polymer dope onto glass plates after which solvent was removed by heating in an oven at 125°C for one hour. The resulting yellow films, which were only lightly converted at this stage, could be stripped from the glass plates. Further cyclization occurred with additional heating. After one hour at 225°, the films were generally blood red in color, while after three hours at 325° the films were black by reflected light but a deep red by transmitted light. The films were clear, tough and moderately flexible at all stages of conversion. The films have excellent tensile strengths while the low elongation and unusually high modulus values are in keeping with their rigid ladder structures.

### Radiation Effects

Since polymers with a highly aromatic structure will in general withstand ionizing radiation, it was expected that the imidazopyrrolone structures would show a high level of radiation resistance. On the basis of preliminary results, the imidazopyrrolones appear to be one of the most radiation-resistant polymers to be developed to date. The data in Table II was obtained on 1 mil films from a PMDA-TADPO polymer.

Table II

### Radiation Effects on PMDA-TADPO Films

<u>Dose</u> <u>(Megarads)</u>	<u>Strength (Kpsi)</u>		<u>Tangent</u> <u>Modulus (Kpsi)</u>	<u>Elongation</u> <u>(%)</u>
	<u>Yield</u>	<u>Tensile</u>		
Control	9.2	17.9	730	9
1,000	12.2	16.8	830	3
5,000	14.3	20.2	820	3
10,000	15.6	17.3	850	3

The doses of one Mev electrons were applied at a rate of 1,000 megarads per hour. Specimens were degassed for 72 hours at 50°C/10<sup>-7</sup> torr and sealed at 10<sup>-7</sup> torr. After an initial effect of solvent expulsion and additional cyclization or conversion, there is clearly no significant effect on film properties even after a 10,000 megarad dose of 1 Mev electrons.

#### Thermal Stabilities

The high degree of radiation stability is undoubtedly due to extensive delocalization which would also be expected to provide exceptional thermal stability to the poly(imidazopyrrolones). From preliminary data, it is believed that the polyimidazopyrrolones are tractable precursors to pyrolytic graphite materials. Figure 3 shows comparative thermogravimetric analyses of a converted pyromellitic dianhydride-diaminobenzidine polymer (PMDA-DAB) and pyrolytic graphite, run in air. It is interesting to note that the maximum rates of weight loss for both materials are nearly identical.

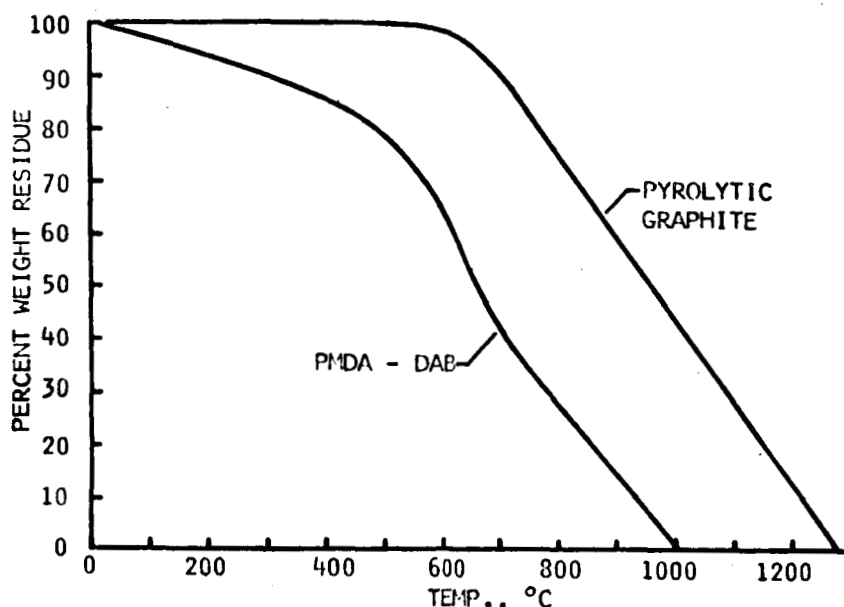


FIGURE 3.- COMPARATIVE THERMOGRAVIMETRIC ANALYSES IN AIR

Figure 4 shows comparative thermogravimetric analyses for two films prepared from a pyromellitic dianhydride-tetraaminodiphenyl ether polymer, at two levels of conversion and a related polyimide film. Apparently the gradual loss of weight of the PMDA-TADPO film 1, which was at an intermediate stage of condensation, results from further conversion as well as solvent loss. This low temperature weight loss is nearly eliminated in the plot of the TGA performed on PMDA-TADPO film 2, which was at an extremely high level of conversion.

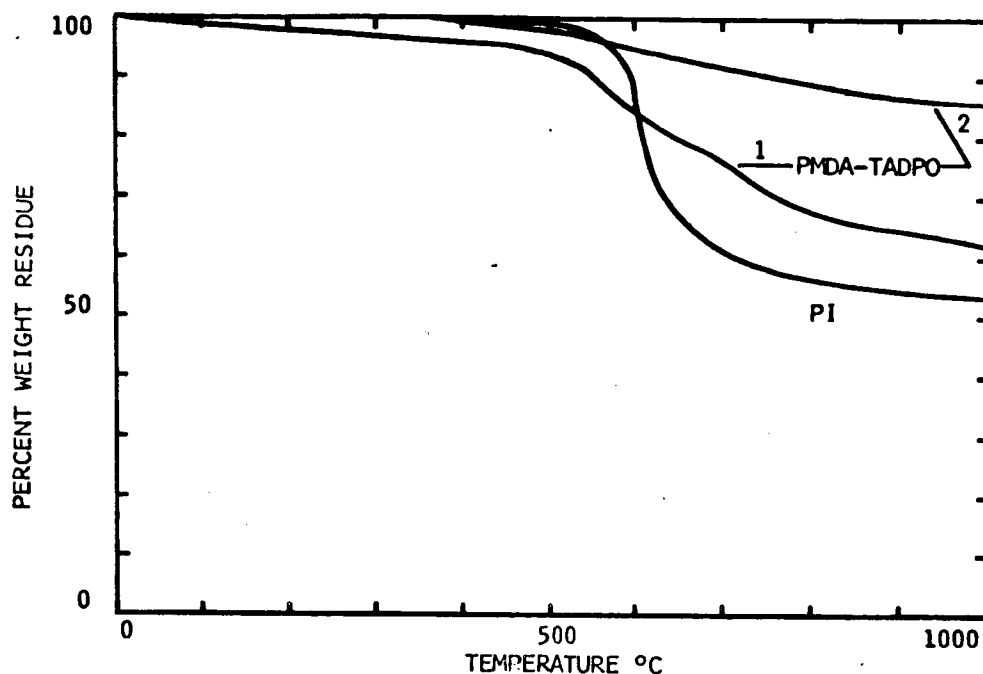


FIGURE 4. - THERMOGRAVIMETRIC ANALYSIS OF A PYRRONE AND POLYIMIDE IN VACUUM

The unusual thermal stability of the imidazopyrrolones is also believed to be reflected in the elemental analyses in which the carbon values for the converted polymers are as much as 7% lower than the theoretical values. The identical analytical procedure gives carbon values 5% lower than theory for pyrolytic graphite, which indicates the inadequacy of the analytical method to degrade the thermally stable polymers. However, nitrogen values are in good agreement with theoretical values, perhaps because the Kjeldahl nitrogen analysis is a chemical analysis, independent of the thermal behavior of the polymers.

The gradual loss of solvent from polymer films at temperatures up to 500°C appears to be one of the most interesting facets of the polyimidazopyrrolone system. A number of experiments point to the existence of an unusually stable complex between these polymers and the highly polar solvents in which they are prepared. Such complexes have previously been isolated and studied for aromatic acids and anhydrides.<sup>8</sup> We assume that the same sort of complex can exist in polymers, especially for the very polar A-A-A polymers, with a high concentration of amide, acid, and amine functional groups. Figure 5 shows plots of power factor loss versus temperature for a PMDA-DAB polymer. This measurement has often been used to measure the glass transition temperature of polymers. In the initial curve 1 the two small peaks at 105-110°C and 330°C may be attributed to loss of water of cyclization and expulsion of tightly-coordinated or reacted solvent, respectively. The results of thermal cycling of the polymer are



shown by curve 2, Figure 5. The apparent glass transition temperature of 475°C is quite unusual and work is in progress to study this phenomenon.

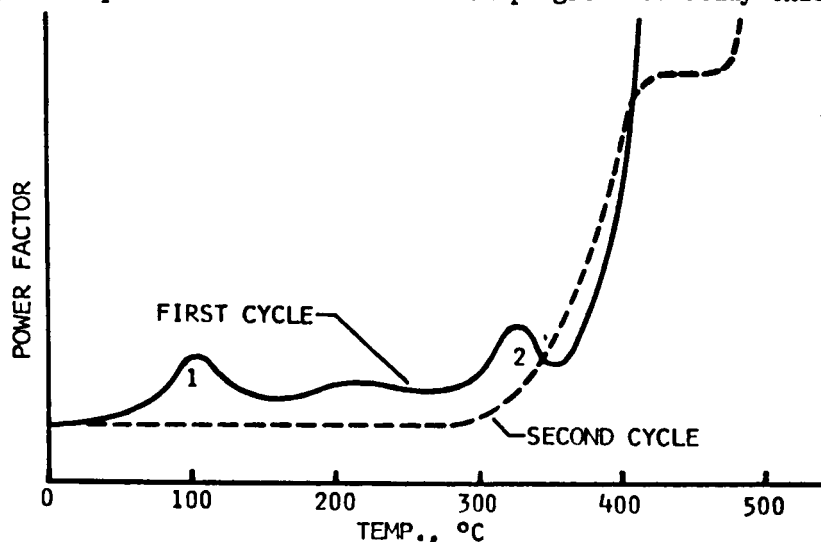


FIGURE 5. - POWER FACTOR VS. TEMPERATURE

Many of the potential applications of the Pyrrones such as films, coatings, and adhesives are being investigated.<sup>11</sup> The A-A-A polymer solution wets fiberglass very well, and filament winding applications are also being studied. Thick glass fabric laminates with good strength have been prepared with resin contents as low as 10%. The prepolymers have been molded into filled and unfilled forms, using high pressures and moderate temperatures. Preliminary indications are that a variety of unique electrical applications may result, since the electrical properties vary at different conversion stages.

## EXPERIMENTAL

### Monomers and Solvents

Pyromellitic dianhydride (PMDA) (Hexagon Laboratories, Inc. and Princeton Chemical Research) was purified by sublimation at 225°/0.5 mm. 3,3',4,4'-Benzophenone tetracarboxylic acid dianhydride (BTDA) (Gulf Chemical Corporation) was sublimed at 240°/0.5 mm.

3,3'-Diaminobenzidine (DAB) (Koppers Chemical Co.) was purified by recrystallization from water with charcoal treatment. 1,2,4,5-Tetraaminobenzene tetrahydrochloride (TAB) (Burdick and Jackson Laboratories, Inc.) was purified by dissolving in the minimum amount of water, treating with charcoal and reprecipitating with concentrated hydrochloric acid. 3,3',4,4'-Tetraaminodiphenyl ether (TADPO) was prepared by a modification<sup>9</sup> of an earlier procedure.<sup>10</sup>

Solvents were purified by distillation from phosphorus pentoxide and, in certain cases, an additional distillation from pyromellitic dianhydride was performed.

### Solution Polycondensation

Poly(Oxy-7H, 15H-2, 10-bis-benzimidazo[1,2-a:1',2'-a'] benzo [1,2-c:4,5-c'] dipyrrol-7, 15-dione)

The general procedure for polymerizing dianhydrides with tetraamines as the free base can be illustrated by the preparation of the polymer from PMDA and TADPO. A solution of 4.20 g. (0.0192 mole) of PMDA in 40 ml. of DMF was added at once to a stirred solution of 4.60 g. (0.020 mole) of 3,3',4,4'-tetraaminodiphenyl ether in 35 ml. of DMF in a Waring blender. The solution thickened slightly and become warm (35-40°) within 15-20 seconds. The stirring was continued for 5-10 minutes after which a portion of a solution of 0.30 g. (0.0014 mole) of PMDA in 5 ml. of DMF was added dropwise to the stirred polymer solution until the desired viscosity was obtained.

A portion of this solution was added to acetone, and the precipitated polymer was collected by filtration, washed well with acetone, and dried under vacuum at room temperature. Calculated for  $(C_{22}H_{16}N_4O_7)_n$  [poly-(amide-acid-amine)]: C, 58.93; H, 3.60; N, 12.50; O, 24.98. Found: C, 56.03; H, 4.34; N, 12.54; O, 25.15. After heating this polymer at 425° for one hour, the analysis was as follows. Calculated for  $(C_{22}H_8N_4O_3)_n$  [the poly(imidazopyrrolone)]: C, 70.21; H, 2.14; N, 14.89; O, 12.76. Found: C, 63.29; H, 2.88; N, 14.77; O, 16.64.

#### Poly(Imidazopyrrolone) from Pyromellitic Dianhydride and 1,2,4,5-Tetraaminobenzene

Since 1,2,4,5-tetraaminobenzene is extremely susceptible to air oxidation, polymers from this tetraamine were prepared using the tetrahydrochloride salt. A solution of 4.36 g. (0.020 mole) of PMDA in 40 ml. of DMF was added slowly, in a dropwise fashion, to a stirred slurry of 5.68 g. (0.020 mole) of the hydrochloride salt in 35 ml. of DMF and 6.32 g. (0.080 mole) of pyridine. The polymerization mixture was blanketed at all times with nitrogen. The resulting viscous polymer solution was utilized as prepared for coatings, films, etc., or the polymer was precipitated by addition of the solution to aqueous ethanol, and washed successively with aqueous ethanol and acetone to remove pyridine hydrochloride, after which it was redissolved in DMF for further characterization.

#### ACKNOWLEDGEMENTS

The authors wish to acknowledge the assistance of Dr. Toshikazu Kurosaki (NAS-NRC Resident Research Associate on leave from Tokyo Institute of Technology) for interpretation of the infrared spectra, Mr. J. B. Nelson and Mr. G. F. Sykes for the thermophysical properties, Dr. L. Monteith (Research Triangle Institute) for electrical properties measurements, Dr. George D. Sands for the solution properties, and Mr. H. H. Heyson for the radiation tests.

# REFERENCES

1. Vogel, H., and C. S. Marvel, J. Polymer Sci., 50, 511 (1961).
2. Sroog, E. E., A. L. Endry, L. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Olivier, J. Polymer Sci., 3A, 1373 (1965).
3. a) Stille, J. K. and J. R. Williamson, J. Polymer Sci., B2, 203 (1964).  
b) Hergenrath, P. M., W. Wrasidlo, H. H. Levine, J. Polymer Sci., 3A, 1665 (1965).  
c) Kubota, T. and R. Nakanishi, J. Polymer Sci., B2, 655 (1964).  
d) Frazer, A. H. and F. T. Wallenberger, J. Polymer Sci., A2, 1157 (1964).
4. Marvel, C. S., Polymer Preprints, American Chemical Society Meeting, Philadelphia, Pa., April 1964.
5. Tessler, M. M., USAF TDR-64-151, July 1964.
6. Porai-Koshits, B. A. and M. M. Antoshul'skaya, J. Gen. Chem. (U.S.S.R.) 13, 339 (1943); [C.A. 38, 1234].
7. Patterson, A. M., "Ring Index", p. 1077, American Chemical Society Monograph No. 84, 1940.
8. Ham, G. E. and A. B. Beindorff, U. S. Patent 2,811,548 (1957);  
b) Bower, G. M. and L. W. Frost, J. Polymer Sci., 1A, 3135 (1963).
9. Bell, V. L. and W. E. Lanford, NASA Technical Note, in press.
10. Foster, R. T. and C. S. Marvel, J. Polymer Sci., 3A, 417 (1965).
11. Bell, V. L. and G. F. Pezdirtz, Proceedings of 8th National Meeting of Society of Aerospace Materials and Process Engineers, San Francisco, California, May 25-28, 1965.